Supporting Information

A Luminescent Polyoxoniobate Lanthanide Derivative

${Eu_{3}(H_{2}O)_{9}[Nb_{48}O_{138}(H_{2}O)_{6}]}^{27-}$

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Contents

- 1. Materials and Methods
- 2. Synthesis and Characterization
- 3. Single-crystal X-ray Crystallography
- 4. Synthetic discussion
- 5. Bond Valence Sum (BVS) Calculations
- 6. The bond angle and the bond distance
- 7. Additional Structural Figures
- 8. ESI-MS (Electrospray Ionization Mass Spectrometry)
- 9. Additional measurements

1. Materials and Methods

 K_7 [HNb₆O₁₉]·13H₂O (Nb₆O₁₉) was synthesized as reported in the literature,^[1] and the other reagents were used as purchased without further purification. Elemental analyses (C, H, N) were performed with a Perkin–Elmer 2400–II CHNS/O analyzer. ICP analyses were carried out on a PerkinElmer Optima 2000 ICP-OES spectrometer. SEM-EDX measurement was performed on a JSM-7610F scaning electron microscope using OXFORD x-act EDX. ESI-MS measurements were performed on an AB SCIEX Triple TOF 4600 spectrometer and data was analyzed using the Peakview 2.0 software provided. The experiments were performed with the negative ion mode in mixed acetonitrile/water (1:3) solvent by direct infusion with a syringe pump with a flow rate of 5 μ L min⁻¹ at 300 °C. Diffuse reflectance spectrum was recorded with a Varian Cary 5000 in the range of 800-200 nm at room temperature. The UV-Vis spectrum was carried out on UV-540 ultraviolet-visible spectrophotometer in the range of 190–900 nm at room temperature. High resolution emission, excitation spectra and the decay curves were obtained on an FLS980 Edinburgh Analytical Instrument apparatus equipped with a 450 W xenon lamp and a µF900H high energy microsecond flash lamp as the excitation sources. IR spectra were obtained from KBr pellets on Perkin Elmer Spectrum Two spectrometer in the 400–4000 cm⁻¹ region. Water contents were determined by TG analyses on a Mettler-Toledo TGA/SDTA 851^e instrument with a heating rate of 10 °C min⁻¹ heated from 25 to 800 °C under nitrogen.

2. Synthesis and Characterization

 $(CN_3H_6)_7K_3H_{17}(Eu_3(H_2O)_9Nb_{48}O_{138}(H_2O)_6)-40H_2O$ (1): Citric acid (0.0263 g, 1.25 umol) and $K_7HNb_6O_{19}\cdot 13H_2O$ (0.171 g, 1.25×10⁻⁴ mol) was added to 10 mL distilled water sequentially with stirring, and the mixture was stirred until the solid was completely dissolved. Then, a solution of EuCl₃·7H₂O (0.0366 g, 1.0 umol, 5 mL distilled water) was added dropwise slowly keeping the mixture solution clear. Ten minutes later, the mixture was adjusted to pH 5.60 with 1M HAc solution and was stirred at 90 °C for 60 min. After being cooled to room temperature, the resulting solution added 0.01 g guanidine hydrochloride was filtered and left to slowly evaporate at room temperature. Over a period of 4 weeks, colorless strip single crystals suitable for single crystal X–ray structure determination were obtained. Yield: 0.04g, ca.29.4% (based on Nb). Elemental analysis calcd (%) for 1: H 1.96, N 3.39, C 0.97, K 1.35, Nb 51.44, Eu 5.26. Found: H 2.05, N 3.51, C 1.17, K 1.43, Nb 50.24, Eu 5.09. IR spectra (KBr pellet): 1657(s), 881(m), 744(s), 654(s) 536(m) and 403(w) cm⁻¹.

3. Single-crystal X-ray Crystallography

A good single crystal of **1** with dimensions of $0.28 \times 0.15 \times 0.13$ mm³ was prudentially picked under an optical microscope and sealed to a glass tube closed at both ends. Intensity data were collected on Bruker APEX–II CCD detector at 296(2) K with Mo K α radiation ($\lambda = 0.71073$ Å). Direct methods were used to solve the structures and to locate the heavy atoms using the *SHELXTL–97* program package. The remaining atoms were found from successive full–matrix least–squares refinements on F^2 and Fourier syntheses.^[2] Lorentz polarization and multi-scan absorption corrections were applied.^[3] In the final refinement, the Nb, Eu and K atoms were refined anisotropically; the disorder K2 atom and all O, C and N atoms were refined isotropically. The guanidine cations and lattice water molecules were all determinated by the results of the element analysis and TGA. The hydrogen atoms of the guanidine groups were placed in calculated positions and then refined using a riding model. All H atoms on water molecules were directly included in the molecular formula. A summary of crystal data and structure refinements for compound **1** is provided in **Table S1**.

	1
Empirical formula	$O_{174}H_{108}Nb_{48}Eu_3C_6N_{18}K_3$
Formula weight	8249.96
CCDC-number	1527359
Crystal system	monoclinic
Space group	C2/c
a [Å]	18.643(1)
b [Å]	38.357(2)
<i>c</i> [Å]	45.950(3)
<i>θ</i> [o]	91.491(1)
V [Å3]	32846(4)
Ζ	4
$ ho_{ m calcd} [m g\cdot cm^{-3}]$	1.668
μ [mm ⁻¹]	2.272
data/parameters	29156/674
R _{int}	0.0423
GOF	1.072
$R_1, wR_2 [I > 2\sigma(I)]$	0.0701, 0.1842
R_1, wR_2 [all data]	0.0934, 0.2048

Table S1. Crystal Data and Structure Refinement for 1

4. Synthetic discussion

The Ln³⁺ ions would hydrolyse into Ln-hydroxides at the slightly higher pH region, in contrary, Nbprecursor K₇HNb₆O₁₉·13H₂O could hydrolyse into Nb₂O₅·nH₂O in acidic solutions. As a result, the important key for synthesis the title compound is to realize coexistence of these reactants in the same system. Firstly, it is important to keep the mixture solution clear. Dilute LnCl₃ solution (A) was added dropwise slowly into the completely clear solution of citric acid and K₇HNb₆O₁₉·13H₂O (B). However, the solution became cloudy if solution B was added into A. Secondly, a lot of parallel experiments indicated that the pH value of the reaction is a determining factor for the isolation of the compound. When the solution A and solution B were completely mixed under stirring after 20 minutes, the pH of the solution was carefully adjusted to approximately 5.60. In addition, if the pH value of the reaction was lower than 5, colloidal unidentified materials were obtained. Finally, the charge balance cations play an important role in forming the compounds. In our experiment, guanidine hydrochloride favors to the formation of the title compound whereas we can't obtain the title compound when the other cations such as Cs⁺, NH₄⁺, (CH₃)₂N⁺, (CH₃)₄N⁺ and [(C₄H₉)₄N]⁺ were used.

5. Bond Valence Sum (BVS) Calculations

Atom	Bond	Valence	Atom	Bond	Valence	Atom	Bond	Valence
Code	Valence	state	Code	Valence	state	Code	Valence	state
Eu1	3.101	+3	Nb8	4.914	+5	Nb17	4.966	+5
Eu2	2.708	+3	Nb9	4.828	+5	Nb18	4.935	+5
Nb1	5.029	+5	Nb10	4.899	+5	Nb19	4.866	+5
Nb2	4.876	+5	Nb11	4.875	+5	Nb20	4.880	+5
Nb3	4.982	+5	Nb12	4.791	+5	Nb21	4.894	+5
Nb4	4.856	+5	Nb13	4.969	+5	Nb22	4.871	+5
Nb5	4.879	+5	Nb14	4.986	+5	Nb23	4.927	+5
Nb6	4.935	+5	Nb15	4.891	+5	Nb24	5.007	+5
Nb7	4.911	+5	Nb16	5.025	+5			

Table S2. The bond valence sum calculations of the Eu and Nb atoms.

Table S3. The bond valence sum calculations of the terminal oxygen atoms in 1a

	Oxygen	Bond	Oxygen	Bond	Oxygen	Bond	Oxygen	Bond
_	Code	Valence	Code	Valence	Code	Valence	Code	Valence
	04	-1.484	024	-1.470	017	-1.568	08	-1.560
	012	-1.486	03	-1.468	016	-1.599	O20	-1.497
	014	-1.444	018	-1.550	013	-1.631		
	01W	-0.286	O2W	-0.281	O3W	-0.288		

Table S4. The bond valence sum calculations of the rest of oxygen atoms in 1a

			10		
Oxygen Code	Bond Valence	Oxygen Code	Bond Valence	Oxygen Code	Bond Valence
O6	-1.677	043	-1.777	01	-1.849
O30	-1.675	O48	-1.741	02	-1.814
037	-1.688	O49	-1.754	O28	-1.852
O40	-1.666	O 50	-1.729	O2 9	-1.851
07	-1.726	051	-1.766	O32	-1.877
09	-1.790	052	-1.772	O34	-1.860
O10	-1.771	053	-1.766	O 35	-1.865
011	-1.737	O54	-1.730	O 36	-1.838
015	-1.745	055	-1.737	O38	-1.884
019	-1.757	057	-1.780	O42	-1.843
021	-1.718	O 58	-1.755	O44	-1.869
022	-1.700	O 59	-1.768	O 45	-1.848
023	-1.798	O60	-1.780	O 46	-1.861
025	-1.719	O62	-1.705	O47	-1.875
O26	-1.770	O63	-1.770	O 61	-1.863
027	-1.728	O64	-1.743	O 65	-1.836
031	-1.796	O66	-1.775	O 67	-1.829
O33	-1.732	O68	-1.783	05	-1.903
O39	-1.767	O69	-1.764	O 56	-1.904
O41	-1.766				

6. The bond angle and the bond distance

Eu–O Bond	Distance/ Å	Eu–OW Bond	Distance/ Å
Eu1–O1 ^A	2.402(7)	Eu1-O4W	2.539(9)
Eu1–O2 ^A	2.392(7)	Eu1-O5W	2.507(9)
Eu1-05	2.377(8)	Eu1-O6W	2.457(10)
Eu1–065 ^D	2.389(8)	Eu2–O7W	2.48(2)
Eu1–067 ^D	2.385(7)	Eu2–O8W	2.56(2)
Eu2–O36	2.394(8)	Eu2–O9W	2.56(2)
Eu2–O42	2.388(8)		
Eu2–O36 ^c	2.366(8)		
Eu2-042 ^c	2.358(8)		
(Eu–O) _{Ave.}	2.383	(Eu–OW) _{Ave.}	2.517

Table S5. The distance of the Eu–O and Eu–O_w

A=(1-x, y, 0.5-z), B=(1+x, y, z), C=(2-x, y, 0.5-z) D= (-1+x, y, z)

7. Additional Structural Figures.



Fig. S1 View of 1D chain of 1 with ganidinium and potassium ions.



Fig. S2 Representation of the two nearest vertex oxygen atoms of {Nb₇O₂₂} linked with Eu³⁺ ions.



Fig. S4 View of the position of Eu1 in 1a. A=(1-x, y, 0.5-z), B=(1+x, y, z), C=(2-x, y, 0.5-z)

Table S6. Assignment of peaks in negative mode mass spectrum					
Observed	Charren	Observed	Calculated	Debuenier	
m/z	Charge	Mass	Mass	Polyanion	
840.8560	9	7567.70	7567.91	${K(CN_{3}H_{6})_{2}H_{15}Eu_{3}(H_{2}O)_{9}[Nb_{48}O_{138}(H_{2}O)_{6}]}^{9-}$	
845.0753	9	7605.68	7606.00	$\{K_2(CN_3H_6)_2H_{14}Eu_3(H_2O)_9[Nb_{48}O_{138}(H_2O)_6]\}^{9-1}$	
945.5715	8	7564.57	7563.95	${K(CN_3H_6)H_{17}Eu_3(H_2O)_{12}[Nb_{48}O_{138}(H_2O)_6]}^{8-}$	
950.4500	8	7603.60	7604.00	$\{K_3(CN_3H_6)H_{15}Eu_3(H_2O)_{10}[Nb_{48}O_{138}(H_2O)_6]\}^{8-1}$	
1097.6561	7	7683.59	7683.05	$\{K(CN_3H_6)_3H_{16}Eu_3(H_2O)_{12}[Nb_{48}O_{138}(H_2O)_6]\}^{7-1}$	
1103.0800	7	7721.56	7721.14	$\{K_2(CN_3H_6)_3H_{15}Eu_3(H_2O)_{12}[Nb_{48}O_{138}(H_2O)_6]\}^{7-1}$	
1283.7590	6	7702.55	7702.07	$\{K(CN_3H_6)_3H_{17}Eu_3(H_2O)_{13}[Nb_{48}O_{138}(H_2O)_6]\}^{6-1}$	
1287.0891	6	7722.53	7722.14	$\{K_2(CN_3H_6)_3H_{16}Eu_3(H_2O)_{12}[Nb_{48}O_{138}(H_2O)_6]\}^{6-1}$	

8. ESI-MS (Electrospray Ionization Mass Spectrometry)



Fig. S5 ESI-MS of $\{Eu_3(H_2O)_9[Nb_{48}O_{138}(H_2O)_6]\}^{27-}$ by varying pH using HAc / KOH.

9. Additional measurements

8.1 IR spectrum

In the IR spectra of **1** and $K_7HNb_6O_{19}\cdot 13H_2O$, the bands at 882 cm⁻¹ is strong and ascribed to Nb–O_t stretching vibrations. The strong and broad bands in the region of 400–800 cm⁻¹ are associated with Nb–O_b vibration frequencies, which was split compared with that of the precursor $K_7HNb_6O_{19}\cdot 13H_2O$.



Fig. S6 IR spectra of 1 (black) and K₇HNb₆O₁₉·13H₂O (red)

8.2 Thermogravimetric analyses

The thermal behavior of **1** has been investigated under nitrogen atmospheres between 25 and 800 °C by thermogravimetric analysis (TGA). The TG curve of **1** exhibits three steps of weight loss in the temperature range 25–800 °C. The first weight loss of 10.17% from 25 to 250 °C is attributed to the loss of 40 lattice water molecules and 9 coordinated water molecules with Eu³⁺ ions (10.15% calculated). The second weight loss from 250 to 540 °C is attributed to the loss of 7 guanidinium caions (4.68% observed, 4.77% calculated). The third step in the region of 540–800°C with a value of 3.78%, which is attributed to the decomposition of the polyoxoanions (3.74% calculated).



Fig. S7 Thermogravimetric analysis (TGA) curve of 1

8.3 Decay curves



Fig. S8 Decay curves of 1 monitored under excitation at 394 nm and emission at 700 nm, 656nm, 619 nm, 594 nm, and 578 nm.

8.4 CIE chromaticity diagram



Fig. S9 CIE chromaticity diagram of the emissions of 1

8.5 UV-VIS spectrum



Fig. S10 The UV-VIS spectrum of 1

A solution composed of freshly dissolved **1** exhibited absorbance maxima at 214 nm, which corresponds to Nb \rightarrow O charge-transfer processes.

8.6 SEM-EDX analysis



The SEM-EDX spectra of ${\bf 1}$ give the compositional information.

References:

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